

CHROMIUM, A DIMER IN SILICATE MELTS?: IMPLICATIONS FOR REDOX EQUILIBRIA AND PARTITIONING; R. O. Colson, Moorhead State University, Moorhead MN and M. C. Colson, Moorhead Junior High School, Moorhead MN.

The redox behavior and partitioning of chromium is important in understanding lunar geochemistry. For example, Cr partitioning has been used to infer the oxidation state of the lunar interior [1]. However, work we report here suggests that, under some conditions, trivalent Cr exists in part as a dimer in silicate melts. This means that both the proportions of trivalent and divalent Cr and the partitioning of trivalent Cr depend on chromium concentration for some range of concentrations. This dependence on concentration has not been taken into account in work to date. We find that tetravalent Sn also exists as a dimer in silicate melts. Simple concentrations of elements or oxides in melts cannot succeed in predicting activities of species when those species are dimers or other species more complex than the simple ions previously supposed to exist in silicate melts.

Existence of Sn dimers in diopsidic melt has been suggested previously, based on electrochemical studies of Sn reduction [2]. We confirm this in a second composition ( $\text{MgO}\cdot\text{CaO}\cdot 1.4\text{SiO}_2$ ). Figure 1 shows a voltammetric curve derived for Sn reduction in this composition. Based on theoretical curves reported in [3] and [4], cathodic and anodic relative peak heights, relative peak positions, and peak shapes are consistent with a monomerization reaction of the type  $\text{Sn(IV)}_2 + 4e^- = 2\text{Sn}^{2+}$ , and inconsistent with other reactions such as a simple 1 electron, 2 electron (e.g.  $\text{Sn(IV)} + 2e^- = \text{Sn}^{2+}$ ), or 4 electron process. The actual melt species associated with the Sn dimer cannot be determined voltammetrically. For a monomerization reaction occurring during reduction, peak positions are expected to change with changing concentration. This shift is shown in Fig. 2.

If Sn exists as a dimer in silicate melts, it is possible other elements do as well. We have done experiments to test whether Cr exists as a dimer. [2, 5] report voltammetry curve shapes for reduction of trivalent to divalent Cr which are inconsistent with a reversible 1 electron reduction, but interpret the curves as arising from reduction of divalent Cr to metallic Cr superimposed on the 1 electron reduction. [2] report a shift in peak position with concentration, an observation consistent with monomerization. We have expanded the experiments of [2] to test for a monomerization reaction.

Figure 3 illustrates that the cathodic Cr voltammetric peak shifts with compositions by nearly the amount expected for a monomerization reaction. A shift in peak position might also accompany a non-reversible reaction, or a reaction in which the activity of metallic Cr depends on its concentration in the Pt electrodes used in the voltammetry experiments (presuming that the peak shape results from the superposition of the reductions of trivalent to divalent Cr and divalent to metallic Cr). However, these conditions would result in changes in peak position with scan rate and deviations from a linear trend when the peak height is plotted against the square root of scan rate. Neither of these occur (Figs. 4 and 5), suggesting that the peak shift is due to monomerization, suggesting in turn that trivalent Cr exists as some dimer species in the melt. This observation is consistent with trivalent Cr ion pairs reported in silicate melts by [6], based on electron paramagnetic resonance (EPR). [6] suggest that the Cr pairs may exist in spinel-like structures in the melt.

Unlike Sn, Cr voltammetry peaks do not fit a theoretical monomerization curve. Rather, there is excess current at low potentials. We interpret this excess current as arising from reduction of a component of trivalent Cr that does not exist as a dimer. This is also consistent with [6]. We have fit the observed voltammetric curves to the sum of a theoretical simple 1 electron reduction of trivalent Cr and a reduction of a trivalent Cr dimer (Fig. 6). As shown, the monomerization provides a significantly better fit to the data than the sum of simple reduction of trivalent Cr followed by the 2 electron reduction of divalent Cr to Cr metal.

Because trivalent Cr exists as both dimer and monomer in the melt, changing the total trivalent Cr concentration changes the proportions of Cr present as dimer and monomer. This is illustrated by considering the reaction  $\text{Cr}_2^{6+} = 2\text{Cr}^{3+}$ . Proportions of trivalent Cr in each state is determined from:  $K = [\text{Cr}^{3+}]^2/[\text{Cr}_2^{6+}]$ . As the total amount of trivalent Cr decreases, the proportion of dimer decreases. We could express redox equilibria using either Cr present as dimer or monomer, however, in either case, the proportions of trivalent and divalent species depends on total Cr concentration. For example, expressing trivalent Cr as the concentration of the monomer:  $\text{CrO}_{1.5} = \text{CrO} + 0.25\text{O}_2$  and  $K = [\text{CrO}][\text{O}_2]^{0.25}/[\text{CrO}_{1.5}]$ . Since the trivalent Cr monomer (represented by  $\text{CrO}_{1.5}$ ) depends on total Cr concentration, so must the divalent Cr concentration. **Thus, redox state of Cr is a function of Cr concentration as well as oxygen fugacity.**

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Partitioning depends on trivalent-divalent proportions, and thus on concentration. In addition, partitioning reactions could be written for Cr analogous to the redox reactions above, illustrating that **Cr partitioning will depend directly on total Cr concentration as well.**

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